

The Impact of Porous Microstructures of Gas Hydrates on Their Macroscopic Properties

Werner F. Kuhs, Georgi Genov, Evgeny Goreschnik, Andreas Zeller and Kirsten S. Techmer
GZG Abt. Kristallographie, Georg-August-Universität Göttingen, Göttingen, Germany

Gerhard Bohrmann
Research Center Ocean Margins, Universität Bremen, Bremen, Germany

ABSTRACT

Methane hydrates from both sub-permafrost and seafloor occurrences show a very particular microstructure as evidenced by scanning electron microscopy. These hydrates are frequently porous, with typical pore sizes ranging from 100 nm to 500 nm and occasionally reaching 1 μm . The pores are predominantly closed with only occasional openings between them, and they are filled with methane gas. The gas-filling will affect the physical properties of gas hydrates. In particular, an increase in the attenuation of elastic waves can be expected. We suggest that the repeatedly observed combination of high seismic velocities and high attenuation in gas hydrate-bearing sediments may well be attributed to the presence of gas in the porous microstructures.

INTRODUCTION

The general picture of a gas hydrate is that of a dense ice-like substance acting as a cement in sedimentary material, although very little is known about the actual microstructures in geological settings. Laboratory-grown gas hydrates of methane, carbon dioxide and nitrogen have been found to be mesoporous to macroporous (Kuks, Klapproth, Gotthardt, Techmer and Heinrichs, 2000). Meanwhile there is accumulated evidence that natural gas hydrates from both continental and seafloor occurrences show identical microstructures. In fact, all natural samples investigated so far by means of cryo-scanning electron microscopy show a very pronounced sub-micron porosity. In particular, samples from Hydrate Ridge (Suess, Bohrmann, Rickert, Kuhs, Torres, Trehu and Linke, 2002) as well as samples from the continental Mallik site, NWT, Canada (Techmer, Heinrichs and Kuhs, 2004) exhibit such porous microstructures together with denser parts. The occurrence of porous microstructures may be indicative for the occurrence of excess free gas during the formation (Staykova, Kuhs, Salamatin and Hansen, 2003). Here, we present the results of microstructural investigations of several marine and continental gas hydrates, comparing the observed structures with laboratory-made material. The comparison should enable us to draw preliminary conclusions on the formation processes of gas hydrates. The analysis of the pore structure by image analysis as well as by specific surface area measurements should provide a first appreciation of porosity's role for the macroscopic properties of gas hydrates. Some of these properties are relevant to a number of geophysical and engineering problems. In particular, the frequently observed anomalous features of seismic signals in gas hydrate horizons, notably the strong attenuation combined with high wave speeds

(e.g. Guerin and Goldberg, 2002), should be considered in the light of the unusual microstructures found in gas hydrates.

We first present the experimental techniques for a microstructural analysis of gas hydrates and show the appearance of marine gas hydrates from a number of different locations as well as continental sub-permafrost hydrates. Based on these observations, we will attempt to quantify the porosity in these hydrates and relate it to the observed macroscopic properties.

EXPERIMENTAL TECHNIQUES

Cryo Electron Microscopy

Gas hydrates need high pressures and/or low temperatures to be stable. Electron microscopic investigations under high vacuum conditions must then be carried out at temperatures below -150°C to avoid sample decomposition. The SEM laboratory at GZG Göttingen features a Field-Emission Scanning Electron Microscope (FE-SEM) combined with an EDX-detector (energy dispersive X-ray detector) for major chemical element analyses. The FE-SEM (LEO Gemini 1530) is a dedicated low-keV system that achieves high resolution even at primary electron energies below 1 keV. It is then possible to run surface studies of samples at low accelerating voltages, thus minimizing beam damage. Additionally, the microscope is equipped with a nitrogen-cooled preparation stage as well as a nitrogen-cooled sample stage in the main chamber, allowing for studies of materials at temperatures down to -185°C . Further treatments, such as fresh cuts of surfaces and/or an additional conductive coating of the surface, may be undertaken in the cryo preparation chamber. However, at the low acceleration voltages <2 keV, the charging of the gas hydrate samples is nearly negligible, making it feasible to look at surfaces without any coating. This also circumvents ambiguities that may arise from the possible generation of artifacts in the coating process. In order to get qualitative elemental analyses by EDX, it was found that the accelerating voltage could be increased for short intervals without significantly modifying the microstructures observed. Thus, beam-sensitive surfaces of ice or gas hydrates can readily be investigated (Kuks,

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Klapproth, Gotthardt, Techmer and Heinrichs, 2000; Klapproth, Goreshnik, Staykova, Klein and Kuhs, 2003; Staykova, Kuhs, Salamatin and Hansen, 2003; Dominé, Lauzier, Cabanes, Legagneux, Kuhs, Techmer and Heinrichs, 2003; Legagneux, Lauzier, Dominé, Kuhs, Heinrichs and Techmer, 2003). It is noteworthy in this context that the charging effects of the uncoated samples' surfaces can be used to distinguish gas hydrates from frozen water; ice Ih shows much higher charging as compared to gas hydrates. Our cryo SEM work on many natural and laboratory-made gas hydrates has corroborated the existence of porosities at a sub-micron level. Below, we will show the ubiquitous occurrence of these microstructures and discuss some possible consequences.

Specific Surface Area Measurements

In order to further characterize these sub-micron porosities, we have constructed an apparatus for measuring the specific surface area (SSA) of gas hydrates, i.e. for materials that are unstable at ambient conditions. Commercially available machines do not work satisfactorily under such circumstances. The specific surface area is determined by methane adsorption measurements performed at liquid N₂ temperature (e.g. Legagneux, Cabanes and Dominé, 2002). The adsorption isotherm is measured using a volumetric method; these data are then analyzed using the BET approach (Brunauer, Emmett and Teller, 1938), thus yielding the total surface area and the adsorption energies. Weighing the samples and normalizing the measured surface ultimately yield the SSA with a reproducibility of 10% to 20%. Most useful are measurements with a given grain size of the gas hydrate particles; such samples can be obtained by sieving the samples in liquid nitrogen. From the grain-size dependency of the measured SSA one can in principle deduce to which extent the pores are open to gas diffusion. This information is crucial for constructing a geometric model of the porous hydrates.

RESULTS

The SEM appearances of natural and laboratory-made methane hydrate samples are very similar. Both show pore sizes of typically 100–500 nm (occasionally reaching 1 μm). SEM images provide a good representation of the surface relief, i.e. essentially 2-dimensional information. In order to learn more about the pore shape and connectivities, we have performed depth-profiling by a controlled sublimation in the SEM. We can deduce from this approach that the pores are of elongated shape with occasional branching. They appear to be separated by walls of variable thickness. There is no preferred orientation of the elongated pores, i.e. the microstructure is essentially isotropic. The geometric surface area as estimated from the SEM micrographs amounts to 50–80 m²/g. First results of a BET analysis on laboratory-made methane hydrates show an SSA of 0.8–1.2 m²/g, indicating that the sub-micron pores are predominantly closed, i.e. only accessible at the grain surface.

Natural Samples

Natural gas hydrate samples were recovered from the seafloor using a TV-grab or gravity corer from various locations: Gas Hydrate Ridge, Cascadia Margin, in the Pacific (Fig. 1a); Yalta mud volcano from the Sorokin Trough, northeastern Black Sea (Fig. 1b); and the southwest African margin off the Congo River (Fig. 1c). The depths below sea-level were approximately 600 m, 2000 m and 3000 m, respectively (Bohrmann, Linke, Suess and Pfannkuche, 2000; Bohrmann and Schenck, 2002; Spiess, Kasten, Schneider, Zuehlsdorf, Bohrmann, Sahling, Breitzke, Bialas

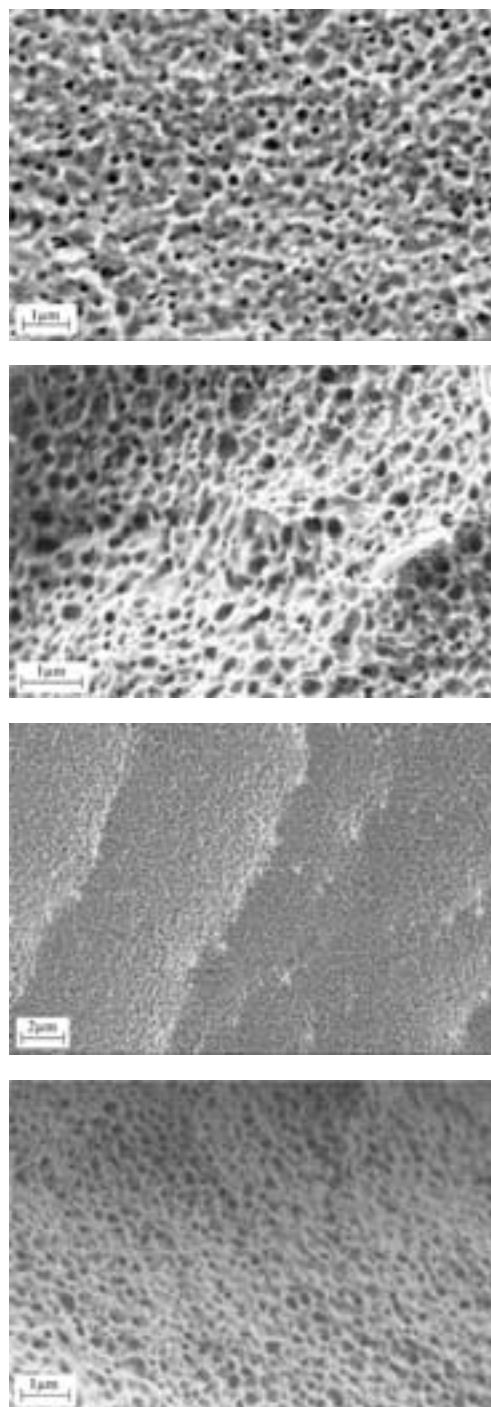


Fig. 1 Electron micrographs of natural gas hydrate samples. Top to bottom: (a) Hydrate Ridge; (b) Black Sea; (c) SW African Margin; (d) Mallik 5L research well, NWT, Canada. Further details in text.

and Ivanov, 2003). Other samples were recovered from the JAPEx/JNOC/GSC Mallik 5-L research well, NWT, Canada at a depth of 800 to 1100 m (i.e. below the lower limit of the permafrost); these samples also show sub-micron porosity (Fig. 1d).

The size of a single crystallite of natural methane hydrate can sometimes be deduced from the particular etching behaviour of grain boundaries observed in the SEM. The typical crystallite size is of a few μm up to a few tens of μm , a rather small size for a material formed at temperatures where its molecular mobilities are quite high. The deduced small crystallite sizes find further support

in our synchrotron X-ray analysis of laboratory-made gas hydrate samples (Klapproth, Goreshnik, Staykova, Klein and Kuhs, 2003).

Most natural samples recovered both from the ocean seafloor or from sub-permafrost continental occurrences have spent some time outside the stability field of gas hydrates. (See also Tulk, Wright, Ratcliffe and Ripmeester, 1999.) The lapse of time between leaving the stability field and sample recovery in liquid nitrogen typically spans 15 to 30 min. During this time partial decomposition takes place. We have identified the corresponding microstructures of the decomposition process (Fig. 2). They are quite distinct from the sub-micron porous microstructures found in the intact material.

Occasionally, the micrographs show the sharp transition between the undecomposed sub-micron porous gas hydrate and dense material with a large number of micron-size pores (Figs. 2a and b). From the surface-charging effect of the electron beam (see above), we can safely attribute the dense material to ice Ih that has formed upon quenching the samples in liquid nitrogen. Likewise, fully decomposed pieces of gas hydrate exhibit microstructures resembling Swiss cheese (Fig. 2c), i.e. dense regions with frequent, larger pores several μm in size. These large pores are likely to be formed during the freezing process of the quenched

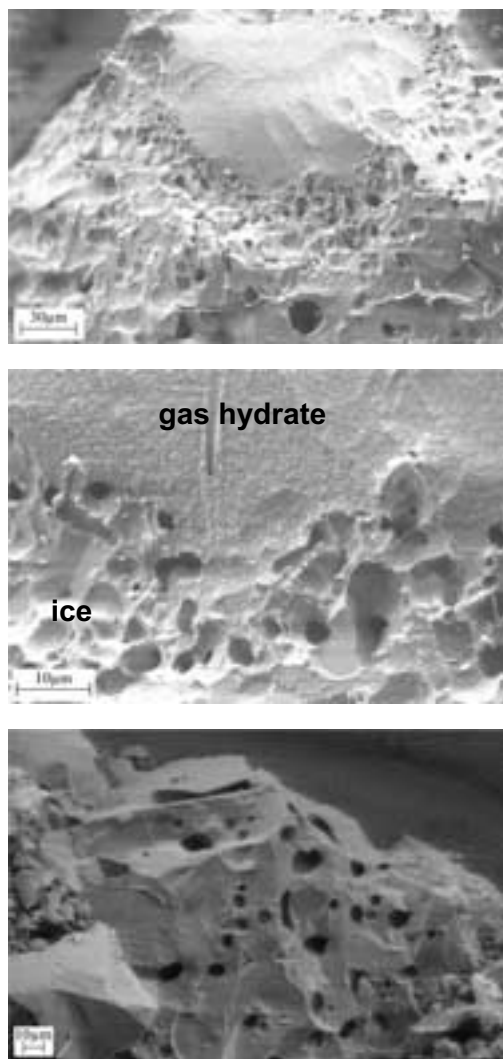


Fig. 2 Microstructural appearance of partially decomposed gas hydrates. Top to bottom: (a) gas hydrate from Sorokin Trough, Black Sea; (b) detail, central part of top figure; (c) decomposed hydrate from Mallik 5L research well. Discussion in text.

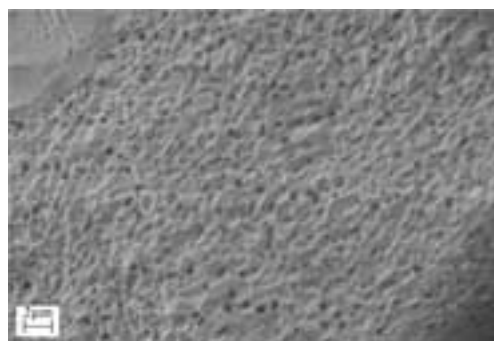


Fig. 3 Laboratory-made hydrate sample formed from ice Ih at -8.8°C and methane pressure of 6 MPa

water, as ice Ih has a very low solubility for methane gas. In addition, a more quantitative estimate of the state of preservation was obtained from X-ray diffraction of a representative part of the sample, using material finely crushed at liquid nitrogen temperatures and analysing the data using a full pattern profile fitting procedure. The quantitative X-ray phase analysis yields the molar ratio of gas hydrate to ice with a precision of a few percent. It is clear that finely dispersed gas hydrates have little chance of surviving the recovery procedure. Only the central parts of massive pieces of gas hydrate can be recovered by the usual TV-grabbing or gravity coring procedures.

Laboratory-made Samples

A large number of synthetic samples was investigated and their formation kinetics were established for a wide range of pressures (up to 0.1 GPa) and temperatures (-80°C to $+5^{\circ}\text{C}$). These resulting microstructures can be compared with those of natural samples. Mostly, pure methane gas was used, but numerous experiments were also conducted with gas mixtures and with pure CO_2 gas. Using the phenomenological growth model of Salamatin and Kuhs (2002), good agreement of theory and experiment can be achieved; a 15%–20% contribution of the sub-micron pore space to the macroscopic volume is consistent with this model (Staykova, Kuhs, Salamatin and Hansen, 2003).

The recovery is much more straightforward in the laboratory and can be usually achieved in less than 1 min and as rapidly as about 10 s. Almost all laboratory-made samples show microstructures that are indistinguishable from those of the natural material (Fig. 3). This suggests that the microscopic growth mechanism is very similar. Likewise, we have performed decomposition experiments under controlled conditions. They were found very useful for identifying microstructural features of decomposition in natural samples.

DISCUSSION

Influence of Sample Recovery

The observation of indistinguishable microstructures for both natural and laboratory-made samples strongly suggests that sub-micron porosity is a typical feature of gas hydrates. That it is not an artifact of the recovery procedure is corroborated by the fact that CO_2 hydrates exhibit a sub-micron porosity formed at temperatures as low as 185 K at gas pressures of a few mbar. The recovery procedure in this case is not problematic, as the hydrate never leaves the stability field down to liquid nitrogen temperatures. From this observation we conclude that the sub-micron porosity of gas hydrates is a typical feature of gas hydrates grown in the presence of free gas; this has recently also been confirmed

by Stern, Kirby, Circone and Durham (2004). The formation of nanometric pores in the SEM was never observed. However, it should be mentioned that larger pores several μm in size are frequently formed when methane-rich water originating from partial decomposition is rapidly frozen to form ice Ih. Some of these microstructures formed upon decomposition are characterized by high porosities, suggesting that a large portion of methane was still dissolved in the water after hydrate decomposition. This is consistent with the observation that gas hydrate decomposition leads to a metastable enrichment of gas in water with concentrations much higher than the values in thermodynamic equilibrium (e.g. Parent and Bishnoi, 1996; Takeya, Hori, Hondoh and Uchida, 2000).

Formation of Sub-micron Porous Hydrates

While it is now well established by our SEM investigations that laboratory-made gas hydrates predominantly exhibit sub-micron porosity (Staykova, Hansen, Salamatin and Kuhs, 2002; Klapproth, Goreschnik, Staykova, Klein and Kuhs, 2003; Staykova, Kuhs, Salamatin and Hansen, 2003), the molecular mechanisms producing this microstructure are still unknown. The sub-micron porosity remains stable over periods of several months at least, as established by earlier laboratory experiments (Kuhs, Klapproth, Gotthardt, Techmer and Heinrichs, 2000). It is clear that for these porous microstructures to remain stable, the pores need to be filled with methane gas, and this will have a number of consequences, as discussed below. This strongly suggests that water molecules cannot easily reach the gas caught in the predominantly closed pores; if this could happen, the remaining gas would react with water and eventually form dense (nonporous) hydrates. Obviously, gas hydrates form an effective barrier to water diffusion, with the consequence that water and free gas may well exist in close vicinity even on an mm scale.

In addition we should note that under certain circumstances dense (nonporous) gas hydrates are also formed in laboratory experiments, in particular at some later stage of the hydrate formation (e.g. Klapproth, Goreschnik, Staykova, Klein and Kuhs, 2003). At present, a final answer cannot be given to the question: Under which growth conditions are porous or dense hydrates formed? It is however noteworthy that the gas hydrate localities of Hydrate Ridge, Cascadia Margin or the Black Sea's Sorokin Trough are linked to the existence of free methane gas (Suess, Torres, Bohrmann, Collier, Rickert, Goldfinger, Linke, Heuser, Sahling, Heeschen, Jung, Nakamura, Greinert, Pfannkuche, Tréhu, Klinkhammer, Whiticar, Eisenhauer, Teichert and Elvert, 2001). From our laboratory experiments we know that free gas (provided in excess with respect to the water available for hydrate formation) leads to predominantly sub-micron porous gas hydrates. It is conceivable that the formation and decomposition kinetics of porous and dense hydrates differ, meriting further studies.

Resulting Macrophysical Properties

From the SEM observations and our growth modelling we have very good evidence that the gas-filled sub-micron pores within natural hydrates occupy an appreciable part of their total volume, amounting at least to 15%–20% (Staykova, Kuhs, Salamatin and Hansen, 2003). Undoubtedly, this will affect the physical properties of gas hydrates in an important way. Thermal properties (conductivity and diffusivity) of sub-micron porous gas hydrates will be lowered and modified as compared to dense hydrate forms considered in the past (Ruppel, 2000). Likewise, the elasto-mechanical properties will be considerably changed, affecting the seismic response of gas hydrates. The intra-crystalline

gas–gas hydrate interface of the porous material will produce some elastic scattering and contribute to the velocity dispersion as well as to a possibly very considerable seismic attenuation. These effects have not yet been included in any modelling of the seismic response of gas hydrates (Dvorkin, Helgerud, Waite, Kirby and Nur, 2000; Gei and Carcione, 2003). We suggest that these dispersion and attenuation effects should be a part of an effective-medium modelling of gas hydrate-sediment composites. It seems that the strong attenuation in gas hydrate-bearing sediments repeatedly observed (Shipley, Houston, Buffler, Shaub, McMillen, Ladd and Worzel, 1979; Guerin, Goldberg and Meltser, 1999; Guerin and Goldberg, 2002) may partly be provoked by the gas-filling in the sub-micron pores. Strong attenuation was also encountered in laboratory experiments on methane hydrate studied by Brillouin scattering, again possibly originating in sub-micron porosities of the samples (Kiefte, Clouter and Gagnon, 1985). It should be mentioned that in some localities the occurrences of larger gas-filled pore spaces could also contribute to the attenuation. However, this effect is less likely for the Mallik site, for which attenuation effects were also reported; this cannot be easily explained by conventional modelling (Guerin, Goldberg and Collett, 2004) and the present-day macroscopic occurrence of free gas is considered to be unlikely here (Bauer, Haberland, Pratt, Ryberg and Weber, 2004). Undoubtedly, further work is needed to quantify the effect of microstructure on seismic properties. Also, for any quantitative description of seismic signals, one also needs a good representation of the contact between sediment grains and gas hydrates. Again, SEM studies appear to be very revealing in this matter (Techmer, Heinrichs and Kuhs, 2004). Unfortunately, we do not know much about these contacts in detail, particularly since undisturbed samples from the seafloor have not been investigated in terms of their microstructure so far. With new pressure-coring technologies and appropriate sub-sampling, however, progress in this field can be expected in the near future.

CONCLUSIONS

By combining scanning electron microscopy and measurements of the specific surface area, it is concluded that natural gas hydrates frequently exhibit sub-micron porosities with predominantly closed pores. A comparison between natural and laboratory-made samples suggests that these microstructures are common features of gas hydrate formation processes from ice and liquid water in a large range of pressures and temperatures. The sub-micron porous nature of gas hydrates will affect physical properties, in particular the elasto-mechanical properties. The seismic response will be affected, notably by increasing the attenuation for which traditional models cannot find a satisfactory explanation. Better seismic modelling will be important for additional quantitative seismic determination of the amount of gas hydrates occurring in seafloor sediments.

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